

# A Field Evaluation to Compare the Performance of Personal Exposure Multi-Pollutant Samplers vs. Federal Method Monitors at a Central Ambient Air Monitoring Station in Steubenville, Ohio

Air Quality IV

September 22-23, 2004, Arlington, VA

S.E. Winter\*, R.A. Bilonick, J.A. Withum, V.B. Conrad,  
R.M. Statnick, S.T. Ebelt, H.H. Suh, P. Koutrakis



# History

- 1997: USEPA promulgated PM<sub>2.5</sub> standards
- NRC recommendations for PM<sub>2.5</sub> science
  - Do measurements at ambient air station reflect personal exposure?
  - Is it PM<sub>2.5</sub>, a component, a co-pollutant, or a combo responsible for the observed adverse health effects?
- Different sampling equipment and methods



# Criteria for Evaluation

- Collocate personal exposure samplers and federal method monitors to compare under equal conditions
- Evaluate for PM<sub>2.5</sub>, components, and co-pollutants
- Quantify instrumental and method parameters
  - Precision
  - Bias
  - Limits of Detection
- Long term field evaluation > SCAMP



# SCAMP

- Steubenville Comprehensive Air Monitoring Program
- Research Team : CONSOL Energy Inc., Harvard School of Public Health, Franciscan University of Steubenville, Ohio University, St. Vincent College, and Wheeling Jesuit University
- Funding: US DOE/NETL, OCDO, EPRI, API, AISI, NMA, NIEHS, EEI, USEPA, CONSOL Energy Inc.



# SCAMP

- Comprised of (2) interdependent programs
  - Outdoor ambient
  - Indoor, personal, and outside the home
- Outdoor
  - FRM PM<sub>2.5</sub> and Federal Equivalent gas analyzers
- Indoor/Personal
  - Multi-pollutant sampler (developed by the Harvard School of Public Health)



# Outdoor Ambient



*$SO_2$ ,  $O_3$ , and  $NO_2$*

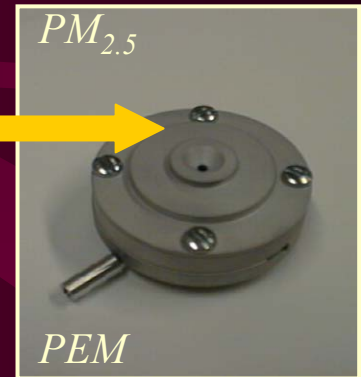
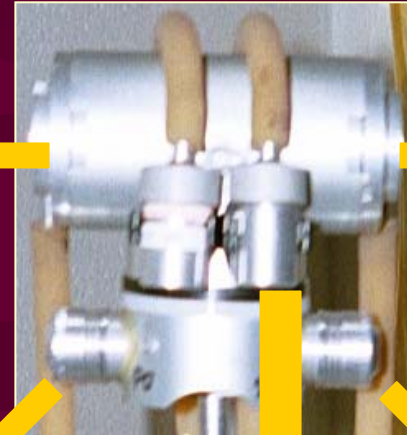
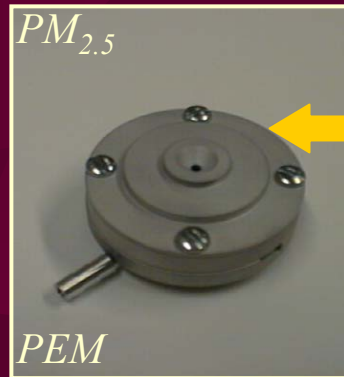


*$PM_{2.5}$  and  $SO_4^{2-}$*





# Indoor, Personal, and Outside



$O_3$ , Ogawa

$SO_2/NO_2$ , Ogawa



# 20 weeks of Collocated Sampling





# Methodology – PM<sub>2.5</sub>

<i>Monitor</i>	<i>Filter–Based or Continuous</i>	<i>Detection</i>	<i>Comments</i>
MP Sampler	Filter – Based, 37 mm Teflon	Gravimetric	<ul style="list-style-type: none"><li>•Collects (2) PM<sub>2.5</sub> filters per MP sampler</li><li>•Flow rate of 4L/min</li></ul>
FRM PM <sub>2.5</sub>	Filter – Based, 47 mm Teflon	Gravimetric	<ul style="list-style-type: none"><li>•Federal Reference Method</li><li>•Flow rate of 16.7L/min</li></ul>



# Methodology – O<sub>3</sub>

<i>Monitor</i>	<i>Filter–Based or Continuous</i>	<i>Detection</i>	<i>Comments</i>
MP Sampler	Filter - Based , Glass fiber filter coated with sodium nitrite/potassium carbonate	Ion Chromatography	• Ogawa Passive Sampling Badge
O <sub>3</sub> Gas Analyzer	Continuous	UV	• Federal Automated Equivalent Method



# Methodology – NO<sub>2</sub>

<i>Monitor</i>	<i>Filter–Based or Continuous</i>	<i>Detection</i>	<i>Comments</i>
MP Sampler	Filter - Based , Cellulose filter coated triethanolamine solution	Ion Chromatography	<ul style="list-style-type: none"><li>• Ogawa Passive Sampling Badge</li><li>• Additional extraction step with H<sub>2</sub>O<sub>2</sub></li></ul>
NO <sub>2</sub> Gas Analyzer	Continuous	Chemiluminescence	<ul style="list-style-type: none"><li>• Federal Automated Reference Method</li></ul>



# Methodology – SO<sub>2</sub>

<i>Monitor</i>	<i>Filter–Based or Continuous</i>	<i>Detection</i>	<i>Comments</i>
MP Sampler	Filter - Based , Cellulose coated triethanolamine solution	Ion Chromatography	<ul style="list-style-type: none"><li>• Ogawa Passive Sampling Badge</li><li>• Additional extraction step with H<sub>2</sub>O<sub>2</sub></li></ul>
SO <sub>2</sub> Gas Analyzer	Continuous	UV Fluorescence	<ul style="list-style-type: none"><li>• Federal Automated Equivalent Method</li></ul>



# Methodology – $\text{SO}_4^{2-}$

<i>Monitor</i>	<i>Filter–Based or Continuous</i>	<i>Detection</i>	<i>Comments</i>
MP Sampler	Filter – Based, Fluoropore filter	Ion Chromatography	<ul style="list-style-type: none"><li>• Mini-PEM operates at a flow of 0.8L/min</li></ul>
FRM $\text{PM}_{2.5}$	Filter – Based, 47 mm Teflon	Ion Chromatography	<ul style="list-style-type: none"><li>• Same filter used to determine mass used to determine sulfate</li><li>• Flow rate of 16.7L/min</li></ul>





# Methodology – Data Analysis

- (Zero) Blank correction to gases not to PM<sub>2.5</sub> or SO<sub>4</sub><sup>2-</sup>
- Limits of Detection were calculated as 3x the SD of blank measurements
- Statistical techniques outlined in Jaech's, Statistical Analysis of Measurement Errors were selected to estimate bias and precision
  - Field evaluation not a controlled lab experiment
  - Samplers of different designs and different methods
    - Precision of equipment was unknown, and ? if one was more precise than the other
  - Use daily pollutant values and not “standards”



# Methodology – Data Analysis

- $Y_{ik} = \alpha_i + \beta_i \mu_k + \varepsilon_{ik}$ 
  - Where  $Y_{ik}$  is the observed concentration for the  $k^{th}$  of  $n$  parcels of air and the  $i^{th}$  of  $N$  samplers
  - $\alpha, \beta$  characterize the relative bias of the  $i^{th}$  sampler
  - $\mu_k$  is the true concentration of  $k^{th}$  air parcel
  - $\varepsilon_{ik}$  is the random error from a Normal distribution with variance  $\sigma_i^2$  for the  $i^{th}$  sampler
- Maximum likelihood estimates –Imprecision Variances and Relative Biases
- Likelihood Ratio tests used to determine if bias was constant or a function of pollutant concentration



# Results - PM<sub>2.5</sub>

- Precision
  - 1.9 (MP Sampler) vs. 2.6  $\mu\text{g}/\text{m}^3$  (FRM)
- Relative Bias
  - 0.2  $\mu\text{g}/\text{m}^3$  when ambient [ ] = 10  $\mu\text{g}/\text{m}^3$
  - 2.0  $\mu\text{g}/\text{m}^3$  when ambient [ ] = 20  $\mu\text{g}/\text{m}^3$
  - 8.7  $\mu\text{g}/\text{m}^3$  when ambient [ ] = 50  $\mu\text{g}/\text{m}^3$
  - Bias changed with concentration
- Limits of Detection
  - 3.0 (MP Sampler) vs. 1.2  $\mu\text{g}/\text{m}^3$  (FRM)



# Results - O<sub>3</sub>

- Precision
  - 5.7 (MP Sampler) vs. 4.1 ppbv (FAE gas analyzer)
- Relative Bias
  - 0.2 ppbv when ambient [ ] = 10 ppbv
  - 2.2 ppbv when ambient [ ] = 25 ppbv
  - 4.8 ppbv when ambient [ ] = 45 ppbv
  - Bias changed with concentration
- Limits of Detection
  - 12.7, 10.7 (MP Sampler) vs. 2.1 ppbv (FAE gas analyzer)



# Results – NO<sub>2</sub>

- Precision
  - 7.0 (MP Sampler) vs. 3.9 ppbv (FAR gas analyzer)
- Relative Bias
  - 2.0 ppbv when ambient [ ] = 5 ppbv
  - 2.0 ppbv when ambient [ ] = 10 ppbv
  - 2.0 ppbv when ambient [ ] = 25 ppbv
  - Bias was constant , did not change with concentration
- Limits of Detection
  - 10.8, 6.1 (MP Sampler) vs. 1.2 ppbv (FAR gas analyzer)





# Results – SO<sub>2</sub>

- Precision
  - 2.5 (MP Sampler) vs. 4.5 ppbv (FAE gas analyzer)
- Relative Bias
  - 6 ppbv when ambient [ ] = 5 ppbv
  - 7.9 ppbv when ambient [ ] = 10 ppbv
  - 13.4 ppbv when ambient [ ] = 25 ppbv
  - 20.7 ppbv when ambient [ ] = 45 ppbv
  - Bias changes with concentration
- Limits of Detection
  - 6.4 (MP Sampler) vs. 2.4ppbv (FAE gas analyzer)



# Results – $\text{SO}_4^{2-}$

- Precision
  - 0.6 (MP Sampler) vs.  $0.9 \mu\text{g}/\text{m}^3$  (FRM)
- Relative Bias
  - $0.0 \mu\text{g}/\text{m}^3$  when ambient [ ] =  $6 \mu\text{g}/\text{m}^3$
  - $0.3 \mu\text{g}/\text{m}^3$  when ambient [ ] =  $8 \mu\text{g}/\text{m}^3$
  - $0.6 \mu\text{g}/\text{m}^3$  when ambient [ ] =  $10 \mu\text{g}/\text{m}^3$
  - Bias changed with concentration
- Limits of Detection
  - 0.2 (MP Sampler) vs.  $0.1 \mu\text{g}/\text{m}^3$  (FRM)



# Summary

- **Particulate Measurements ( $\text{PM}_{2.5}$ ,  $\text{SO}_4^{2-}$ )**
  - **The MP sampler was comparable to the FRM sampler.**
    - Precision and LOD were approximately equal.
    - Bias was approximately 10% for  $\text{PM}_{2.5}$  and 5% for  $\text{SO}_4^{2-}$  at the average ambient concentration.
  - **Similar sampler design and methodology.**



# Summary

- **Gaseous Measurements ( $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ )**
  - **Results were mixed.**
    - **For  $\text{O}_3$  and  $\text{NO}_2$ ,**
      - Biases were approximately 10% at the average ambient concentration.
      - However, LODs for the MP sampler were approximately 5 to 10x higher than the federal gas analyzers and 50% or greater of the average ambient concentration.
      - High blanks for  $\text{O}_3$  and  $\text{NO}_2$  passive sampling.
    - **For  $\text{SO}_2$ ,**
      - Precision and LOD were comparable.
      - However there existed a large bias ( 50% or greater) between the MP sampler and the federal gas analyzer.
      - Reasons for large  $\text{SO}_2$  Bias ?



# Considerations

- SO<sub>2</sub> Bias
  - Ogawa reports good correlation with SO<sub>2</sub> gas analyzer
- Start times were not always correlated
- LODs were slightly higher but practically the same as a lab evaluation of the MP sampler
  - Development and Laboratory Performance Evaluation of a Personal Multipollutant Sampler for Simultaneous Measurements of Particulate and Gaseous Pollutant. *Aerosol Science and Technology*, Volume 35, Issue No. 3 2001.
- Comparison did not include carbon and elements

